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(54) Middle distillate compositions with improved cold flow properties.

(57) The low temperature properties of a distillate petroleum
fuel oil boiling in the range 120°C to 500°C, and whose 20%
and 90% distillation points differ by less than 100°C, and/or
whose Final Boiling Point is in the range 340°C to 370°C are
improved by the addition of a polymer or copolymer having at
least 25 wt. % of n-alkyl groups of average number of carbon
atoms from 12 to 14 with no more than 10 wt. % containing
more than 14 carbon atoms.

EP 0 153 176 A2

Middle Distillate Compositions with Improved Cold Flow
Properties

1 Mineral oils containing paraffin wax have the characteristic
of becoming less fluid as the temperature of the oil
decreases. This loss of fluidity is due to the
crystallization of the wax into plate-like crystals which
eventually form a spongy mass entrapping the oil therein.

5
10 It has long been known that various additives act as wax
crystal modifiers when blended with waxy mineral oils.
These compositions modify the size and shape of wax crystals
and reduce the adhesive forces between the crystals and
between the wax and the oil in such a manner as to permit
the oil to remain fluid at a lower temperature.

15 Various pour point depressants have been described in the
literature and several of these are in commercial use. For
example, U.S. Pat. No. 3,048,479 teaches the use of
copolymers of ethylene and C₃-C₅ vinyl esters, e.g.
vinyl acetate, as pour depressants for fuels, specifically
heating oils, diesel and jet fuels. Hydrocarbon polymeric
pour depressants based on ethylene and higher alpha-olefins,
e.g. propylene, are also known. U.S. Patent 3,961,916
teaches the use of a mixture of copolymers, one of which is
a wax crystal nucleator and the other a growth arrestor to
control the size of the wax crystals.

20
25 United Kingdom Patent 1263152 suggests that the
size of the wax crystals may be controlled by using a
copolymer having a lower degree of side chain branching.

1 It has also been proposed in for example United Kingdom Patent
1469016 that the copolymers of di-n-alkyl fumarates and
vinyl acetate which have previously been used as pour
depressants for lubricating oils may be used as co-additives
5 with ethylene/vinyl acetate copolymers in the treatment of
distillate fuels with high final boiling points to improve
their low temperature flow properties. According to United
Kingdom Patent 1469016 these polymers may be C₆ to C₁₈
alkyl esters of unsaturated C₄ to C₈ dicarboxylic acids
10 particularly lauryl fumarate and lauryl-hexadecyl fumarate.
Typically the materials used are mixed esters with an
average of about 12 carbon atoms (Polymer A). It is notable
that the additives are shown not to be effective in the
"conventional" fuels of lower Final Boiling Point (Fuels III
15 and IV).

United States Patent 3252771 relates to the use of polymers
of C₁₆ to C₁₈ alpha-olefines obtained by polymerising olefin
mixtures that predominate in normal C₁₆ to C₁₈
alpha-olefines with aluminium trichloride/alkyl halide
20 catalysts as pour point and cloud point depressants in
distillate fuels of the broad boiling, easy to treat types
available in the United States in the early 1960's.

With the increasing diversity in distillate fuels, types of
fuel have emerged which cannot be treated by the existing
25 additives or which require an uneconomically high level of
additive to achieve the necessary reduction in their pour
point and control of wax crystal size for low temperature
filterability to allow them to be used commercially. One
particular group of fuels that present such problems are
30 those which have a relatively narrow, and/or low boiling
range. Fuels are frequently characterised by their Initial
Boiling Point, Final Boiling Point and the interim
temperatures at which certain volume percentages of the

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1 initial fuel have been distilled. Fuels whose 20% to 90%
distillation point differ within the range of from 70 to
100°C and/or whose 90% boiling temperature is
from 10 to 25°C of the final boiling point and/or whose
5 final boiling points are between 340 and 370°C have been
found particularly difficult to treat sometimes being
virtually unaffected by additives or otherwise requiring
very high levels of additive. All distillations referred to
herein are according to ASTM D86.

10 With the increase in the cost of crude oil, it has also
become important for a refiner to increase his production of
distillate fuels and to optimise his operations using what
is known as sharp fractionation again resulting in distil-
late fuels that are difficult to treat with conventional
15 additives or that require a treat level that is unacceptably
high from the economic standpoint. Typical sharply fract-
ionated fuels have a 90% to final boiling point range of
10 to 25°C usually with a 20 to 90% boiling range of less
than 100°C, generally 50 to 100°C. Both types of fuel have
20 final boiling points above 340°C generally a final boiling
point in the range 340°C to 370°C especially 340°C to 365°C.

The copolymers of ethylene and vinyl acetate which have
found widespread use for improving the flow of the
previously widely available distillate fuels have not been
25 found to be effective in the treatment of the narrow boiling
and/or sharply fractionated fuels described above.
Furthermore use of mixtures as illustrated in United Kingdom
Patent 1469016 have not been found effective.

We have found however that polymers and copolymers
30 containing very specific alkyl groups, such as specific
di-n-alkyl fumarate/vinyl acetate copolymers, are effective
in both lowering the pour point of the difficult to treat

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1 fuels described above and controlling the size of the wax
2 crystals to allow filterability including those fuels
3 of the lower final boiling point in which the additives of
4 United Kingdom Patent 1469016 were ineffective.

5 Specifically we have found that the average number of carbon
6 atoms in the alkyl groups in the polymer or copolymer must
7 be from 12 to 14 and that no more than 10 wt.% of the alkyl
8 groups should contain more than 14 carbon atoms and
9 preferably no more than 20 wt.% of the alkyl groups contain
10 fewer than 12 carbon atoms. These polymers are particularly
11 effective when used in combination with other low
12 temperature flow improvers which on their own are
13 ineffective in these types of fuels.

14 The present invention therefore provides the use for
15 improving the flow properties of a distillate petroleum fuel
16 oil boiling in the range 120°C to 500°C, whose 20% and 90%
17 distillation points differ by less than 100°C, and/or for
18 improving the flow properties of a distillate fuel whose 90%
19 to final boiling point range is 10 to 25°C and/or whose
20 Final Boiling Point is in the range 340°C to 370°C of an
21 additive comprising a polymer containing at least 25 wt.% of
22 n-alkyl groups, the average number of carbon atoms in the
23 n-alkyl groups is from 12 to 14 and no more than 10 wt.% of
24 the alkyl groups contain more than 14 carbon atoms and
25 preferably no more than 20 wt.% of the alkyl groups contain
fewer than 12 carbon atoms.

26 The additives are preferably used in an amount from 0.0001
27 to 0.5 wt.%, preferably 0.001 and 0.2 wt.% based on the
28 weight of the distillation petroleum fuel oil, and the
29 present invention also includes such treated distillate
30 fuel.

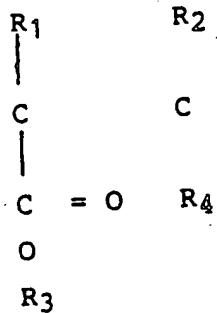
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1 The preferred polymer is a copolymer containing at
 5 least 25 preferably at least 50 wt.% more preferably from 75
 10 to 90 wt.% of a di-n alkyl ester of a dicarboxylic acid
 15 containing alkyl groups containing an average of 12 to 14
 20 carbon atoms and 10 to 50 wt.% of another unsaturated ester
 25 such as a vinyl ester and/or an alkyl acrylate, methacrylate
 fumarate and vinyl acetate are particularly preferred.

10 The polymers or copolymers used in the present invention
 15 preferably have a number average molecular weight in the
 range of 1000 to 100,000, preferably 1,000 to 30,000 as
 measured, for example, by Vapor Pressure Osmometry.

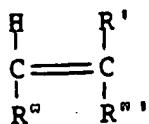
15 The carboxylic acid esters useful for preparing the
 preferred polymer can be represented by the general
 formula:



20 where in R_1 and R_2 are hydrogen or a C_1 to C_4 alkyl
 group, e.g., methyl, R_3 is the C_{12} to C_{14} average,
 straight chain alkyl group, and R_4 is COOR_3 , hydrogen or
 a C_1 to C_4 alkyl group, preferably COOR_3 . These may
 be prepared by esterifying the particular mono- or
 25 di-carboxylic acid with the appropriate alcohol or mixture
 of alcohols.

1 Other unsaturated esters, which can be copolymerized are the
C₁₂-C₁₄ alkyl acrylates and methacrylates.

5 The dicarboxylic acid mono or di- ester monomers may be
copolymers with various amounts, e.g., 5 to 70 mole %, of
other unsaturated esters or olefins. Such other esters
include short chain alkyl esters having the formula:



10 where R' is hydrogen or a C₁ to C₄ alkyl group, R'' is
-COOR''' or -OOOCR''' where R''' is a C₁ to C₅ alkyl group
branched or unbranched, and R''' is R'' or hydrogen. Examples
of these short chain esters are methacrylates, acrylates,
the vinyl esters such as vinyl acetate and vinyl propionate
15 being preferred. More specific examples include methyl
methacrylate, isopropenyl acetate and butyl and isobutyl
acrylate.

20 Our preferred copolymers contain from 40 to 60 mole % of a
C₁₂-C₁₄ average dialkyl fumarate and 60 to 40 mole % of
vinyl acetate.

Where ester polymers or copolymers are used they may
conveniently be prepared by polymerising the ester monomers
in a solution of a hydrocarbon solvent such as heptane,
benzene, cyclohexane, or white oil, at a temperature
25 generally in the range of from 20°C to 150°C and usually
promoted with a peroxide or azo type catalyst, such as
benzoyl peroxide or azodi-isobutyronitrile, under a
blanket of an inert gas such as nitrogen or carbon dioxide,
in order to exclude oxygen.

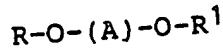
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1 The additives of the present invention are particularly effective when used in combination with other additives known for improving the cold flow properties of distillate fuels generally, although they may be used on their own to impart a combination of improvements to the cold flow behaviour of the fuel.

10 The additives of the present invention are particularly effective when used with the polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two C₁₀ to C₃₀ linear saturated alkyl groups and a polyoxyalkylene glycol group of molecular weight 100 to 5,000 preferably 200 to 5,000, the alkyl group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials form 15 the subject of European Patent Publication 0061895 A2.

The preferred esters, ethers or ester/ethers useful in the present invention may be structurally depicted by the formula:



20 where R and R¹ are the same or different and may be

(i) n-Alkyl



(ii) n-Alkyl - C



(iii) n-Alkyl -O-C-(CH₂)_n-



(iv) n-Alkyl -O-C-(CH₂)_n-C-

30

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1 the alkyl group being linear and saturated and containing 10
2 to 30 carbon atoms, and A represents the polyoxyalkylene
3 segment of the glycol in which the alkylene group has 1 to 4
4 carbon atoms, such as a polyoxymethylene, polyoxyethylene or
5 polyoxytrimethylene moiety which is substantially linear;
some degree of branching with lower alkyl side chains (such
as in polyoxypropylene glycol) may be tolerated but it is
preferred the glycol should be substantially linear.

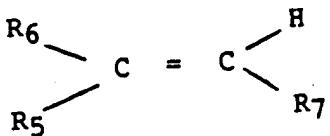
Suitable glycals generally are the substantially linear
10 polyethylene glycals (PEG) and polypropylene glycals (PPG)
having a molecular weight of about 100 to 5,000 preferably
about 200 to 2,000. Esters are preferred and fatty acids
containing from 10-30 carbon atoms are useful for reacting
with the glycals to form the ester additives and it is
15 preferred to use a C₁₈-C₂₄ fatty acid, especially
behenic acids, the esters may also be prepared by
esterifying polyethoxylated fatty acids or polyethoxylated
alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and
20 mixtures thereof are suitable as additives with diesters
preferred for use in narrow boiling distillates whilst minor
amounts of monoethers and monoesters may also be present and
are often formed in the manufacturing process. It is
25 important for additive performance that a major amount of
the dialkyl compound is present. In particular stearic or
behenic diesters of polyethylene glycol, polypropylene
30 glycol or polyethylene/polypropylene glycol mixtures are
preferred.

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1 The additives of this invention may also be used with the
 ethylene unsaturated ester copolymer flow improvers. The
 unsaturated monomers which may be copolymerized with
 ethylene, include unsaturated mono and diesters of the
 general formula:



5 wherein R_6 is hydrogen or methyl; a R_5 is a $-OOCR_8$ group
 10 wherein R_8 is hydrogen or a C_1 to C_{28} , more usually C_1 to
 C_{17} , and preferably a C_1 to C_8 , straight or branched chain
 alkyl group; or R_5 is a $-COOR_8$ group wherein R_8 is as
 previously described but is not hydrogen and R_7 is hydrogen
 or $-COOR_8$ as previously defined. The monomer, when R_5 and
 15 R_7 are hydrogen and R_6 is $-OOCR_8$, includes vinyl alcohol
 esters of C_1 to C_{29} , more usually C_1 to C_{18} , monocarboxylic
 acid, and preferably C_2 to C_5 monocarboxylic acid. Examples
 of vinyl esters which may be copolymerised with ethylene
 include vinyl acetate, vinyl propionate and vinyl butyrate
 or isobutyrate, vinyl acetate being preferred. We prefer
 20 that the copolymers contain from 20 to 40 wt.% of the
 vinyl ester more preferably from 25 to 35 wt.% vinyl ester.
 They may also be mixtures of two copolymers such as those
 described in United States Patent 3961916.

25 It is preferred that these copolymers have a number average
 molecular weight as measured by vapor phase osmometry
 of 1000 to 6000, preferably 1000 to 3000,

30 The additives of the present invention may also be used in
 distillate fuels in combination with polar compounds, either
 ionic or nonionic, which have the capability in fuels of
 acting as wax crystal growth inhibitors. Polar nitrogen
 containing compounds have been found to be especially

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1 effective when used in combination with the glycol esters,
ethers or ester/ethers and such three component mixtures are
within the scope of the present invention. These polar
compounds are generally amine salts and/or amides formed by
5 reaction of at least one molar proportion of hydrocarbyl
substituted amines with a molar proportion of hydrocarbyl
acid having 1 to 4 carboxylic acid groups or their
anhydrides; ester/amides may also be used contain 30 to 300
preferably 50 to 150 total carbon atoms. These nitrogen
10 compounds are described in U.S. Patent 4,211,534. Suitable
amines are usually long chain C₁₂-C₄₀ primary, secondary,
tertiary or quarternary amines or mixtures thereof but
shorter chain amines may be used provided the resulting
nitrogen compound is oil soluble and therefore normally
15 containing about 30 to 300 total carbon atoms. The nitrogen
compound preferably contains at least one straight chain
C₈-C₄₀ preferably C₁₄ to C₂₄ alkyl segment.

Suitable amines include primary, secondary, tertiary or
quaternary, but preferably are secondary. Tertiary and
20 quarternary amines can only form amine salts. Examples of
amines include tetradecyl amine, cocoamine, hydrogenated
tallow amine and the like. Examples of secondary amines
include dioctadecyl amine, methyl-behenyl amine and the
like. Amine mixtures are also suitable and many amines
25 derived from natural materials are mixtures. The preferred
amine is a secondary hydrogenated tallow amine of the
formula HNR₁R₂ wherein R₁ and R₂ are alkyl groups
derived from hydrogenated tallow fat composed of
approximately 4% C₁₄, 31% C₁₆, 59% C₁₈.

30 Examples of suitable carboxylic acids for preparing these
nitrogen compounds (and their anhydrides) include
cyclo-hexane 1,2 dicarboxylic acid, cyclohexene dicarboxylic
acid, cyclopentane 1,2 dicarboxylic acid, naphthalene

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1 dicarboxylic acid and the like. Generally these acids will
have about 5-13 carbon atoms in the cyclic moiety. Preferred
acids useful in the present invention are benzene
5 dicarboxylic acids such as ortho-phthalic acid,
para-phthalic acid, and meta-phthalic acid. Ortho-phthalic
acid or its anhydride is particularly preferred.
10 The particularly preferred compound is the amide-amine salt
formed by reacting 1 molar portion of phthalic anhydride
with 2 molar portions of di-hydrogenated tallow amine.
Another preferred compound is the diamide formed by
15 dehydrating this amide-amine salt.

The relative proportions of additives used in the
mixtures are from 0.5 to 20 parts by weight of the polymer
of the invention containing the n-alkyl groups containing an
average of 12 to 14 carbon atoms to 1 part of the other
15 additives such as the polyoxyalkylene esters, ether or
ester/ether, more preferably from 1.5 to 9 parts by weight
of the polymer of the invention.

20 The additive systems of the present invention may
conveniently be supplied as concentrates for incorporation
into the bulk distillate fuel. These concentrates may also
contain other additives as required. These concentrates
preferably contain from 3 to 75 wt.%, more preferably 3 to
25 60 wt.%, most preferably 10 to 50 wt.% of the additives
within the scope of the present invention.

25 The present invention is illustrated by the following
Examples in which the effectiveness of the additives of the
present invention as pour point depressants and
filterability improvers were compared with other similar
30 additives in the following tests.

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1 By one method, the response of the oil to the additives was
measured by the Cold Filter Plugging Point Test (CFPP)
which is carried out by the procedure described in detail
in "Journal of the Institute of Petroleum", Volume 52,
Number 510, June 1966, pp. 173-185. This test is designed
5 to correlate with the cold flow of a middle distillate in
automotive diesels.

In brief, a 40 ml sample of the oil to be tested is cooled
in a bath which is maintained at about -34°C to give
non-linear cooling at about 1°C/min. Periodically (at each
10 one degree Centigrade drop in temperature starting from at
least 2°C above the cloud point) the cooled oil is tested
for its ability to flow through a fine screen in a
prescribed time period using a test device which is a
15 pipette to whose lower end is attached an inverted funnel
which is positioned below the surface of the oil to be
tested. Stretched across the mouth of the funnel is a 350
mesh screen having an area defined by a 12 millimetre
diameter. The periodic tests are each initiated by applying
a vacuum to the upper end of the pipette whereby oil is
20 drawn through the screen up into the pipette to a mark
indicating 20 ml of oil. After each successful passage the
oil is returned immediately to the CFPP tube. The test is
repeated with each one degree drop in temperature until the
oil fails to fill the pipette within 60 seconds. This
25 temperature is reported as the CFPP temperature. The
difference between the CFPP of an additive free fuel and of
the same fuel containing additive is reported as the CFPP
depression by the additive. A more effective flow
improver gives a greater CFPP depression at the same
30 concentration of additive.

1 Another determination of flow improver effectiveness is
made under conditions of the flow improver distillate
operability test (DOT test) which is a slow cooling test
designed to correlate with the pumping of a stored heating
5 oil. In this test the cold flow properties of the described
fuels containing the additives were determined by the DOT
test as follows. 300 ml of fuel are cooled linearly at
1°C/hour to the test temperature and the temperature then
held constant. After 2 hours at the test temperature,
10 approximately 20 ml of the surface layer is removed as the
abnormally large wax crystals which tend to form on the
oil/air interface during cooling. Wax which has settled in
the bottle is dispersed by gentle stirring, then a CFPP
filter assembly is inserted. The tap is opened to apply a
15 vacuum of 500 mm of mercury, and closed when 200 ml of fuel
have passed through the filter into the graduated
receiver. A PASS is recorded if the 200 ml are collected
within ten seconds through a given mesh size or a FAIL if
the flow rate is too slow indicating that the filter has
20 become blocked.

CFPP filter assemblies with filter screens of 20, 30, 40,
60, 80, 100, 120, 150, 200, 250 and 350 mesh number are
used to determine the finest mesh (largest mesh number) the
fuel will pass. The larger the mesh number that a wax
25 containing fuel will pass, the smaller are the wax crystals
and the greater the effectiveness of the additive flow
improver. It should be noted that no two fuels will give
exactly the same test results at the same treatment level
for the same flow improver additive.

30 The Pour Point was determined by two methods, either the
ASTM D 97 or a visual method in which 100 ml samples of fuel
in a 150 ml narrow necked bottle containing the additive
under test, are cooled at 1°C/hour from 5°C above the wax

1 appearance temperature. The fuel samples were examined at
 3°C intervals for their ability to pour when tilted or
 inverted. A fluid sample (designated F) would move readily
 on tilting, a semi-fluid (designated semi-F) sample may need
 5 to be almost inverted, while a solid sample (designated S)
 can be inverted with no movement of the sample.

The fuels used in these Examples were:

ASTM-D-86 Distillation, °C

Fuel	Wax Appearance Point	Initial	20%	90%	Final Boiling Point
		Boiling Point			
A	-5	202	270	328	343
B	-2	202	254	340	365
C	-2.5	274	286	330	348
D	-4	155	215	335	358
E	-1.5	196	236	344	365

The Additives used were as follows:

Additive 1: A polyethylene glycol of 400 average molecular weight esterified with 2 moles of behenic acid.

20 Additive 2: A copolymer of a mixed C₁₂/C₁₄ alkyl fumarate obtained by reaction of 50:50 weight mixture of normal C₁₂ and C₁₄ alcohols with fumaric acid and vinyl acetate prepared by solution copolymerisation of a 1 to 1 mole ratio mixture at 60°C using azo diisobutyronitrile as catalyst.

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1 The results in the CFPP and Pour Point tests were as follows:
 ASTM D 97

		Fuel	Additive	Amount ppm	CFPP	CFPP Depression	Pour Point
5	A	None			-5°C		-9°C
			1	500	-8°C	3°C	-6°C
			2	500	-3°C	-2°C	-15°C
			2:1	300:200	-9°C	4°C	-18°C
			2:1	600:400	-11°C	6°C	-18°C
					-4°C		-6°C
10	B	None					-6°C
			1	120			-6°C
			1	300	-8°C	4°C	
			2	180			-15°C
			2	300	-2°C	-2°C	
			2:1	180/120	-11°C	7	-18°C
15			2:1	300/200	-13°C	9	-21°C
					-4°C		-6°C
			C	None			-3°C
			1	500	-8°C	4	
			1	1000	-7°C	3	
			2	1000	-2°C	-2	
20			2:1	300/200	-6°C	2	-12°C
			2:1	600/400	-10°C	6	-15°C

The additives of the invention were compared in the DOT test with Additive 3 which was an oil solution containing 63 wt.% of a combination of polymers comprising 13 parts by weight of an ethylene/vinyl acetate copolymer of number average molecular weight 2500 and vinyl acetate content of 36 wt.% and 1 part by weight of a copolymer of ethylene and vinyl acetate of number average molecular weight 3500 and a vinyl acetate content of about 13 wt. %.

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DOT Testppm of additive to pass DOT (120 mesh) at -10°C

Fuel	Additive 3	Mixture of 3 Parts of 1 and 2 Parts of 2
5 A	>3,000	700
B	800	250
C	1,500	700
D	1,250	500
E	>1,500	300

10 Various fumarate/vinyl acetate copolymers were tested in
 admixture (3 parts) with Additive 1 (2 parts) to determine
 the effect of the chain length in the fumarate with the
 following results.

Fuel	Alcohols used to make fumarate	Average C Number in fumarate	Pour Point	CFPP	Depression
			Test	500 at -10°C	1,000 ppm(ai) ppm (ai)
15	A	8	S	2	3
	C-9	9	-	2	-
	C-10	10	S	3	3
	C-10/C-12	11	S	3	4
	C-11	11	-	3	3
	C-12	12	S	3	4
	C-12/C-14	13	F	5	7
	C-14	14	F	-2	-2

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1.	Fuel	Alcohols used to make fumarate	Average C Number in fumarate	Pour Point	CFPP Depression
				Test	Appearance at -10°C
				300	ppm

	B				
5.	C-8	8	S	3	
	C-9	9	-	5	
	C-10	10	S	4	
	C-10/C-12	11	S	5	
	C-11	11	-	5	
10	C-12	12	S	3	
	C-12/C-14	13	F	7	
	C-14	14	F	0	

				1,000	
				ppm	
				3	
15	C	C-10	10	3	
		C-10/C-12	11	3	
		C-11	11	3	
		C-12	12	6	
		C-12/C-14	13	0	
20		C-14	14	3	
		C-18	18		

Various fumarate/vinyl acetate copolymers obtained from different alcohols but averaging 12 to 13.5 carbon atoms in the alkyl groups were tested in the same mixture as in the previous example in the CFPP and Visual pour point tests with the following results.

		Fuel A	Fuel B	Fuel C
		CFPP 500 PPM	CFPP 300 PPM	CFPP Pour Point Depression 300 PPM
		Depression 1000 PPM	500 PPM	Pour Point Depression 1000 PPM
		Appearance at -10°C	Appearance at -10°C	Appearance at -10°C
		C-number	BPM	BPM
1.	C-12/C-14 = 1/1	13.0	5	7
2.	C-12/C-14 = 3/1	12.5	2	4
3.	C-12/C-14 = 1/3	13.5	0	1
4.	C-10/C-16 = 1/1	13.0	-2	-1
5.	C-13 oxo (from tetrapropylene)	13.0	3	-
6.	C-12/C-14/C-16 = 2/1/1	13.5	1	-
7.	C-12/C-14/C-16 = 8/3/1	12.7	4	7
8.	C-8/C-10/C-12/C-14/C-16/C-18 = 9/11/36/30/10/4	12.2	4	6
9.	Ditto = 3/8/33/37/12/8	13.0	0	1
10.	C-12/C-14/C-16/C-18 = 45/38/12/5	13.4	0	0
11.	C-8 to C-18 = 13/10/41/15/9/13	12.5	2	3

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- 1 The fuels B and C were used in the following Examples
together with

Fuel F	ASTM D-86 Distillation °C				FBP
	IBP	20%	50%	90%	
	182	254	285	324	343

- 5 The results are CFPP and visual Pour Point results shown for
various additives in the following table. Where the
additive has no pour depressing effect the CFPP value is not
measured because without pour depression the fuel cannot be
10 used.

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Fuel BCFPP Depression

Additive	400 ppm Fumarate vinyl acetate	400 ppm fumarate/vinyl acetate
Alcohol content of Pumarate	100 ppm Additive 1	100 ppm Additive 1 100 ppm Additive 3
C ₄)		2
C ₄)		2
C ₆)		2
C ₈)	No pour depression*	2
C ₉)		2
C ₁₀)		2
C ₁₁)		2
C ₁₂)		8
C ₁₃)	7°C	
C ₁₃)	0	2
C ₁₄)	Raised by 2°C	Raised by 2°C
C ₁₆)	No pour depression*	
C ₁₈)		
C ₂₂)		
Mixed C ₁₂ /C ₁₄		
3:1	No effect	2
1:1	8°C	9
1:3	4°C	5
C ₁₈ /C ₁₆		
1:1	Raised by 1°C	Raised by 1°C
C ₁₀ /C ₁₂	No effect	2

* No pour depression observed at -10°C after the 1°C/hour cool.

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CFPP Depression

Additive	<u>Fuel C</u>	<u>Fuel F</u>	
	800 ppm F/VA 200 ppm Additive 1	800 ppm F/VA 200 ppm Additive 1	800 ppm F/VA
			200 ppm 1 100 ppm 3

Alcohol content of
Fumarate

C ₄)			
C ₆)			
C ₈)			
C ₉)			
C ₁₀)			
C ₁₁)		9	4
C ₁₂)	3	1	1
C ₁₃)	0	2	1
C ₁₄)	0		-
C ₁₆)	No pour depression*		-
C ₁₈)			-
C ₂₂)			-

Mixed C ₁₂ /C ₁₄			
3:1	No pour depression*	10	1
1:1	4	4	8
1:3	1		4

C ₁₈ /C ₁₆	0	0	1
1:1			
C ₁₀ /C ₁₂			2

No pour depression*

*No pour depression observed at -10°C after the 1 hour cool

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1. The Additives were also tested in combination with Additive 4 the half amide formed by reacting two moles of hydrogenated tallow amine with phthalic anhydride and the CFP Depressions in Fuel B were as follows

	Additive	CFPP Depressions
5	Additive 4 (250 ppm)	6
	Additive 3 (100 ppm)	
	C ₁₂ /C ₁₄ F/VA (250 ppm)	
10	Additive 4 (300 ppm)	6
	Additive 1 (100 ppm)	
	C _{12E} /C ₁₄ F/VA (100 ppm)	
	Additive 4 (250 ppm)	0
	C ₁₂ /C ₁₄ F/VA (250 ppm)	

1 CLAIMS

1 The use for improving the low temperature properties of a distillate petroleum fuel oil boiling in the range 120°C to 500°C, and whose 20% and 90% distillation points differ by less than 100°C, and/or whose 90% to 5 final boiling point range is 10 to 25°C and/or whose Final Boiling Point is in the range 340°C to 370°C of an additive comprising a polymer or copolymer containing at least 25 10 atoms in the n-alkyl groups wherein the average number of carbon wt.% of n-alkyl groups is from 12 to 14 and no more than 10 wt.% of alkyl groups containing more than 14 carbon atoms.

2 A distillate petroleum fuel oil according to claim 1 in which no more than 20 wt.% of the alkyl group 15 contains fewer than 12 carbon atoms.

3 The use according to claim 1 or claim 2 in which the polymer is of a di-n-alkyl ester of a mono-ethylenically unsaturated C₄ to C₈ or dicarboxylic acid.

4 The use according to any of the preceding claims 20 in which the copolymer is of a di-n alkyl ester of dicarboxylic acid in which the alkyl groups containing an average of 12 to 14 carbon atoms and from 10 to 50 wt.% of a vinyl ester, an alkyl acrylate or methacrylate.

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1 5 The use according to any of the preceding claims
as a co-additive with a polyoxyalkylene ester, ether,
ester/ether and mixtures thereof, containing at least two
C₁₀ to C₃₀ linear saturated alkyl groups and a
5 polyoxyalkylene glycol of molecular weight 100 to 5,000
preferably 200 to 5,000, the alkyl group in said
polyoxylakylene glycol containing from 1 to 4 carbon atoms.

6 The use according to any of the preceding claims
in combination with polar compounds, either ionic or
10 nonionic, which have the capability in fuels of acting as
wax crystal growth inhibitors.

7 The use according to Claim 6 in which the polar
compounds are the amine salts and/or amides formed by
reaction of at least one molar proportion of
15 hydrocarbyl-substituted amines with a molar proportion of
hydrocarbyl acid having 1 to 4 carboxylic acid groups or
their anhydrides containing a total of 30 to 300 carbon
atoms.

8 A distillate petroleum fuel oil boiling in the
range 120°C to 500°C and whose 20% and 90% distillation
20 points differ by less than 100°C, and/or whose 90% to final
boiling point is 10 to 25°C and/or whose Final Boiling Point
is in the range 340°C to 370°C containing from 0.001 to 0.5
wt.% of a polymer or copolymer containing at least 25 wt.%
25 of n-alkyl groups wherein the average number of carbon atoms
in the n-alkyl groups is from 12 to 14, there being present
no more than 10 wt.% of alkyl groups containing more than 14
carbon atoms.

0 : 1 9 A distillate petroleum fuel oil according to Claim
8 in which the copolymer is of a di-n alkyl ester of a
dicarboxylic acid in which the alkyl groups containing an
average of 12 to 14 carbon atoms and from 10 to 50 wt.% of a
5 vinyl ester, alkyl acrylate or methacrylate.

10 10 A distillate petroleum fuel oil according to
Claim 8 or Claim 9 containing as a co-additive a
polyoxyalkylene ester, ether, ester/ether and mixtures
thereof, containing at least two C₁₀ to C₃₀ linear
10 saturated alkyl groups and a polyoxyalkylene glycol of
molecular weight 100 to 5,000 preferably 200 to 5,000, the
alkyl group in said polyoxyalkylene glycol containing from 1
to 4 carbon atoms.

11 11 A distillate petroleum fuel oil according to Claim
20 10 containing from 0.5 to 20 parts by weight of the ester
copolymer per part of the polyoxyalkylene ester, ether or
ester/ether.

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1 CLAIMS FOR AUSTRIA

1 A process for improving the low temperature properties of a distillate petroleum fuel oil boiling in the range 120°C to 500°C, and whose 20% and 90% distillation points differ by less than 100°C, and/or whose 90% to final boiling point range is 10 to 25°C and/or whose Final Boiling Point is in the range 340°C to 370°C comprising adding thereto a polymer or copolymer containing at least 25 wt.% of n-alkyl groups wherein the average number of carbon atoms in the n-alkyl groups is from 12 to 14 and no more than 10 wt.% of alkyl groups containing more than 14 carbon atoms.

2 A process according to claim 1 in which no more than 20 wt.% of the alkyl group contains fewer than 12 carbon atoms.

3 A process according to claim 1 or claim 2 in which the polymer is of a di-n-alkyl ester of a mono-ethylenically unsaturated C₄ to C₈ or dicarboxylic acid.

4 A process according to any of the preceding claims in which the copolymer is of a di-n alkyl ester of dicarboxylic acid in which the alkyl groups containing an average of 12 to 14 carbon atoms and from 10 to 50 wt.% of a vinyl ester, an alkyl acrylate or methacrylate.

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1 5 A process according to any of the preceding claims
as a co-additive with a polyoxyalkylene ester, ether,
ester/ether and mixtures thereof, containing at least two
C₁₀ to C₃₀ linear saturated alkyl groups and a
19 5 polyoxyalkylene glycol of molecular weight 100 to 5,000
preferably 200 to 5,000, the alkyl group in said
polyoxyalkylene glycol containing from 1 to 4 carbon atoms.

6 A process according to any of the preceding claims
in combination with polar compounds, either ionic or
10 nonionic, which have the capability in fuels of acting as
wax crystal growth inhibitors.

7 A process according to Claim 6 in which the polar
compounds are the amine salts and/or amides formed by
reaction of at least one molar proportion of
15 hydrocarbyl-substituted amines with a molar proportion of
hydrocarbyl acid having 1 to 4 carboxylic acid groups or
their anhydrides containing a total of 30 to 300 carbon
atoms.

8 A process according to any of the preceding claims
20 in which from 0.001 to 0.5 wt.% of the polymer or copolymer.
is added.



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(54) Middle distillate compositions with improved cold flow properties.

(57) The low temperature properties of a distillate petroleum fuel oil boiling in the range 120°C to 500°C, and whose 20% and 90% distillation points differ by less than 100°C, and/or whose Final Boiling Point is in the range 340°C to 370°C are improved by the addition of a polymer or copolymer having at least 25 wt.% of n-alkyl groups of average number of carbon atoms from 12 to 14 with no more than 10 wt.% containing more than 14 carbon atoms.

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Application number

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EUROPEAN SEARCH REPORT

EP 85 30 1047

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-2 305 492 (EXXON) * Claims 1-3,7-10,12-14; page 7, line 7 - page 8, line 18; page 8, line 27 - page 9, line 18; page 13, lines 16-31; page 16, line 33 - page 17, line 18; page 18, lines 20-23; page 20, examples 7,12 *	1,2,8	C 10 L 1/18
X	--- FR-A-2 305 493 (EXXON) * Claims 1-3,7,9,10; page 7, line 7 - page 7, line 18; page 8, line 27 - page 9, line 18; page 13, lines 16-31; page 15, line 39 - page 16, line 18; page 17, lines 1-23; page 9, examples 5,9 *	1,2,8	
X	--- GB-A- 573 364 (STANDARD OIL DEV.) * Claims 1-3; page 1, lines 54-90 *	1,2,10	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
X	--- US-A-3 413 103 (D.W. YOUNG) * Claims 1,4-6; column 2, lines 8-35; column 2, line 50 - column 3, line 13 *	1-4,8, 9	C 10 L
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The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 09-08-1985	Examiner ROTSART L.D.C.	

CATEGORY OF CITED DOCUMENTS

- IPO FORM 1500.02.82
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
D,X	GB-A-1 469 016 (EXXON) * Claims 1,5,7,8; page 3, lines 1-53; page 4, lines 32-50; page 6, lines 44-55; page 7, lines 17-20 *	1-4,8, 9	
D,A	US-A-4 211 534 (N. FELDMAN) * Claims 1,3-6,13; column 4, line 46 - column 5, line 55; column 7, line 59 - column 9, line 65 *	1-4,8, 9	
Y	---	6	
A	EP-A-0 061 894 (EXXON) * Claims 1,5-10,11,13-14,17; page 21, example 17 *	1,6,7, 8	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP-A-0 061 895 (EXXON) * Claims 1-11,14,16-22 *	1,5-8, 10,11	

The present search report has been drawn up for all claims.			
Place of search THE HAGUE	Date of completion of the search 09-08-1985	Examiner ROTSAERT L.D.C.	
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